

We claim:

1. A method of modifying a polypyrrolic macrocycle, said method comprising

5 reacting said macrocycle with a carbonyl ylide capable of forming a cyano containing macrocycle under refluxing conditions to produce a cyano containing compound, and

reducing a cyano group of said compound with a reducing agent to produce an amine group.

10 2. The method of claim 1 wherein said carbonyl ylide is tetracyanoethylene oxide (TCNEO).

3. The method of claim 1 wherein said macrocycle is a photosensitizer.

15 4. The method of claim 3 wherein said photosensitizer is a porphyrin.

5. The method of claim 4 wherein said porphyrin is a tetraphenylporphyrin (TPP) or a diphenylporphyrin (DPP).

20 6. The method of claim 1 wherein said reducing agent is lithium aluminum hydride.

7. A method of modifying a polypyrrolic macrocycle, said method comprising

25 reacting said macrocycle with a carbonyl ylide capable of forming a cyano containing macrocycle under refluxing conditions to produce a cyano containing compound, and

hydrolyzing a cyano group of said compound to produce an acid or carboxylate moiety.

8. The method of claim 7 further comprising derivatization of said acid or carboxylate moiety to be an ester, amide, or thioamide.

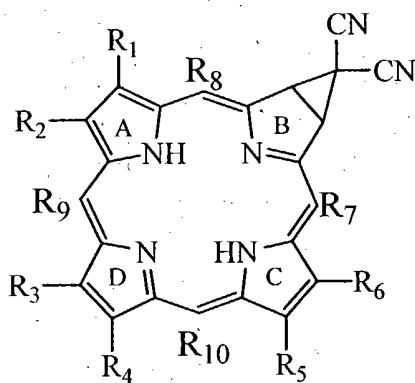
9. The method of claim 7 wherein said carbonyl ylide is tetracyanoethylene oxide (TCNEO).

10. The method of claim 7 wherein said macrocycle is a photosensitizer.

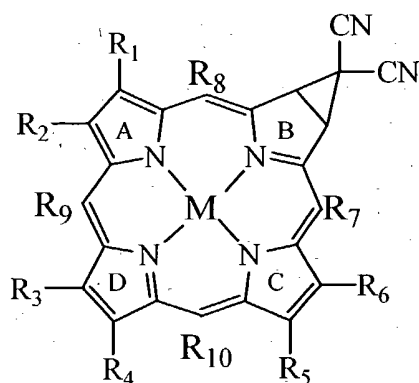
11. The method of claim 10 wherein said photosensitizer is a porphyrin.

12. The method of claim 11 wherein said porphyrin is a tetraphenylporphyrin (TPP) or a diphenylporphyrin (DPP).

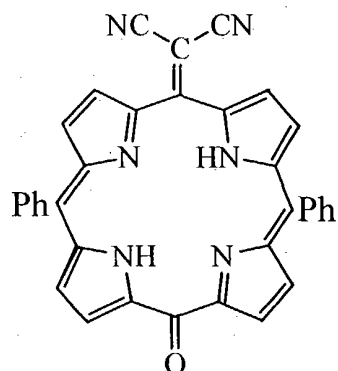
13. The method of claim 1 wherein said cyano containing compound has a structure represented by one of formulas III, IV, (1), (2), (3) or (4) below



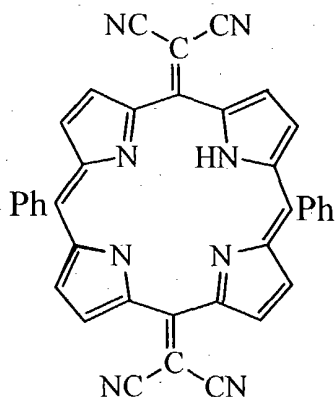
III



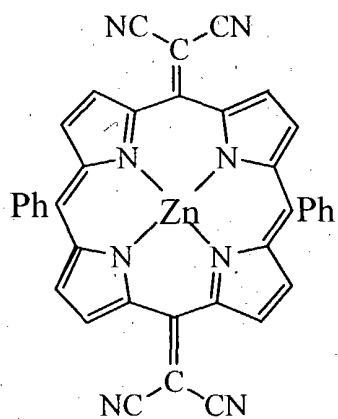
IV



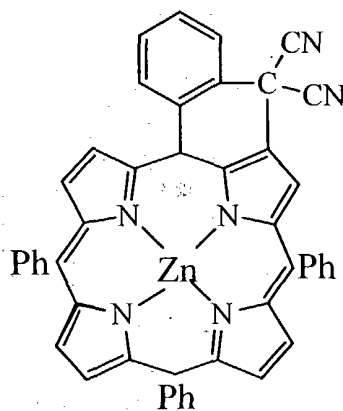
(1)



(2)



(3)



(4)

or

wherein

M is a metal selected from the group consisting of Ni(II), Cu(II), Zn, Sn, Ge, Si, Ga, Al, Mn(III), Gd(III), In and Tc;

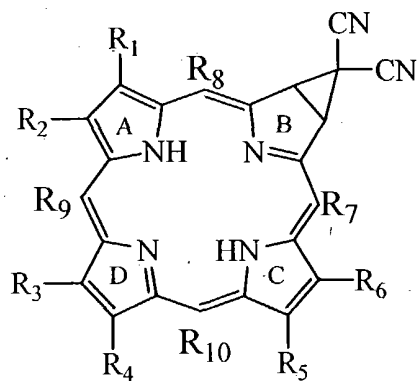
R<sub>1</sub> through R<sub>6</sub> are independently a hydrogen atom, a lower alkyl group, a lower alkyl carboxylic acid or acid ester group, keto, hydroxy, nitro, amino, or a group that, taken together with another pyrrolic ring, ring substituent or meso-substituent, forms a fused 5- or 6-membered ring; and

each of R<sub>7</sub> through R<sub>10</sub> is independently selected from H, substituted or unsubstituted alkyl groups, or substituted or unsubstituted aromatic rings,

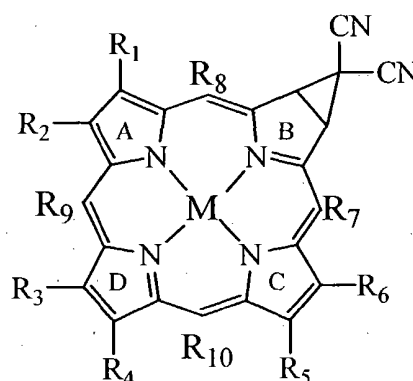
or substituted or unsubstituted cycloalkyl groups, which may be the same or different; and

Ph is phenyl.

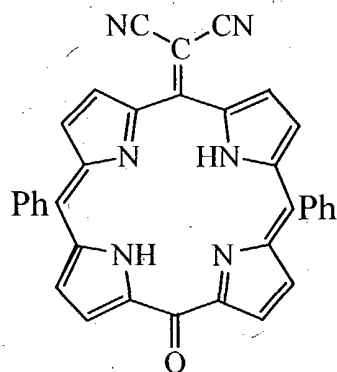
14. The method of claim 7 wherein said cyano containing compound has a structure represented by one of formulas III, IV, (1), (2), (3) or (4) below



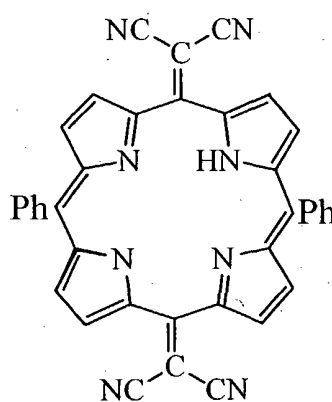
**III**



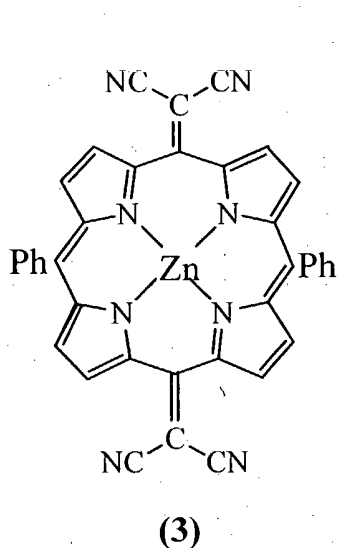
**IV**



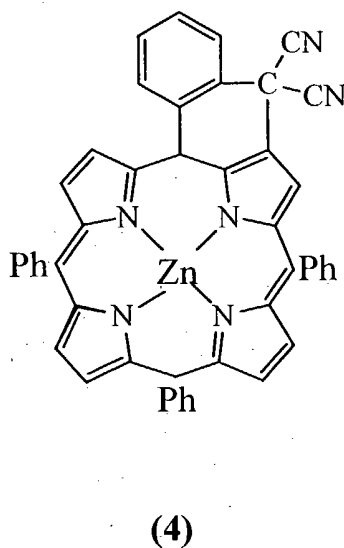
**(1)**



**(2)**



or



wherein

15 M is a metal selected from the group consisting of Ni(II), Cu(II), Zn, Sn, Ge, Si, Ga, Al, Mn(III), Gd(III), In and Tc;

20  $R_1$  through  $R_6$  are independently a hydrogen atom, a lower alkyl group, a lower alkyl carboxylic acid or acid ester group, keto, hydroxy, nitro, amino, or a group that, taken together with another pyrrolic ring, ring substituent or meso-substituent, forms a fused 5- or 6-membered ring; and

each of  $R_7$  through  $R_{10}$  is independently selected from H, substituted or unsubstituted alkyl groups, or substituted or unsubstituted aromatic rings, or substituted or unsubstituted cycloalkyl groups, which may be the same or different; and

Ph is phenyl.

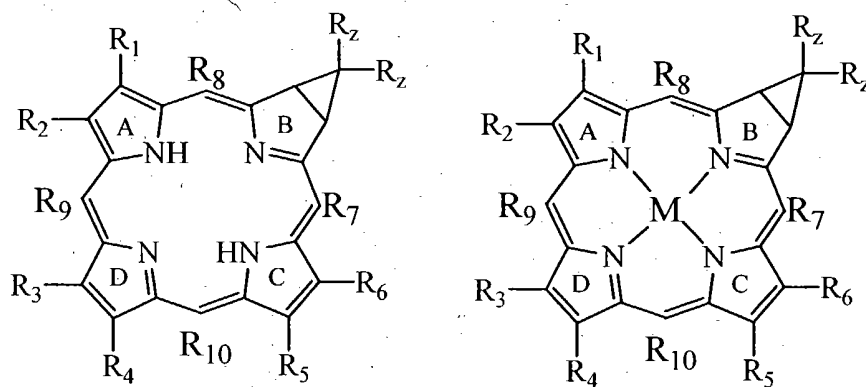
15. A compound produced by the method of claim 1.

25 16. A compound produced by the method of claim 6.

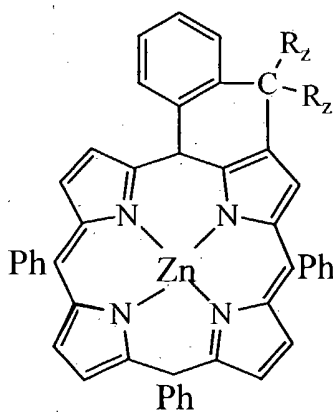
17. A compound produced by the method of claim 7.

18. A compound produced by the method of claim 8.

19. The compound of claim 16 having a structure represented by one of the following formulas



or

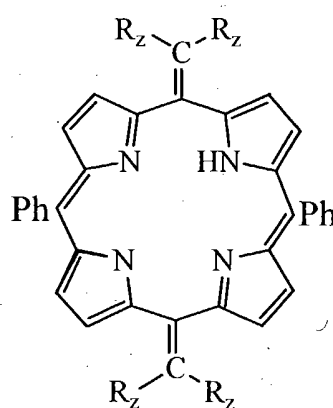
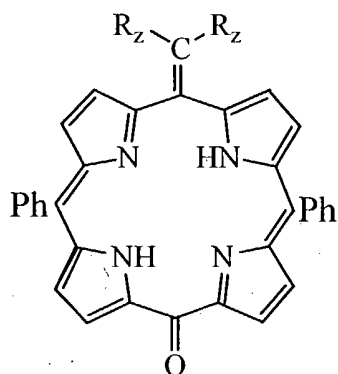
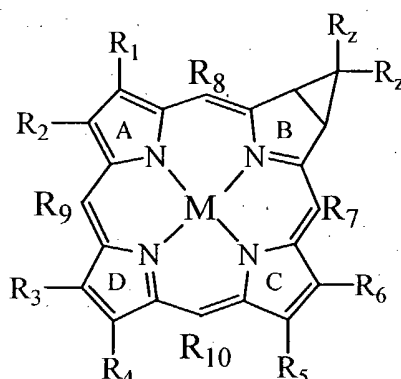
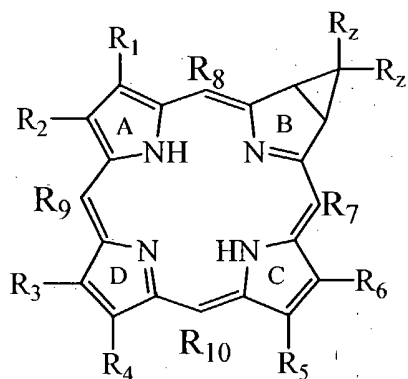


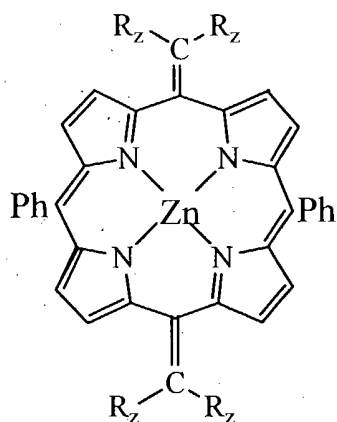
wherein

M is a metal selected from the group consisting of Ni(II), Cu(II), Zn, Sn, Ge, Si, Ga, Al, Mn(III), Gd(III), In and Tc;

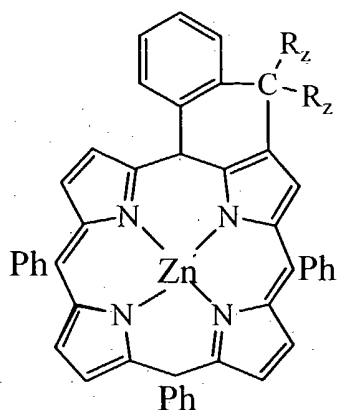
$R_1$  through  $R_6$  are independently a hydrogen atom, a lower alkyl group, a lower alkyl carboxylic acid or acid ester group, keto, hydroxy, nitro, amino, or a group that, taken together with another pyrrolic ring, ring substituent or meso-substituent, forms a fused 5- or 6-membered ring; and  
 each of  $R_7$  through  $R_{10}$  is independently selected from H, substituted or unsubstituted alkyl groups, or substituted or unsubstituted aromatic rings, or substituted or unsubstituted cycloalkyl groups, which may be the same or different; and  
 Ph is phenyl and  $-R_z$  is  $-CN$  where one or more  $-R_z$  is  $-CH_2NH_2$  resulting from reduction of said  $-CN$ .

20. The compound of claim 17 having a structure represented by one of the following formulas





or



wherein

- 10 M is a metal selected from the group consisting of Ni(II), Cu(II), Zn, Sn, Ge, Si, Ga, Al, Mn(III), Gd(III), In and Tc;
- R<sub>1</sub> through R<sub>6</sub> are independently a hydrogen atom, a lower alkyl group, a lower alkyl carboxylic acid or acid ester group, keto, hydroxy, nitro, amino, or a group that, taken together with another pyrrolic ring, ring substituent or
- 15 meso-substituent, forms a fused 5- or 6-membered ring; and
- each of R<sub>7</sub> through R<sub>10</sub> is independently selected from H, substituted or unsubstituted alkyl groups, or substituted or unsubstituted aromatic rings, or substituted or unsubstituted cycloalkyl groups, which may be the same or different; and
- 20 Ph is phenyl and -R<sub>z</sub> is -CN where one or more -R<sub>z</sub> is -COOH resulting from hydrolysis of said -CN.